

RHODIUM-TUNGSTEN ALLOYS FOR HIGH TEMPERATURE ELECTRODES DEPOSITED BY PHOTOLYTIC CHEMICAL VAPOR DEPOSITION

M.A. Ryan, A. Kisor, R.M. Williams,
B. Jeffries-Nakamura, and D. O'Connor

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

Electrodes used in solid electrolyte devices such as high temperature fuel cells and direct conversion devices such as the alkali metal thermal-to-electric converter (AMTEC) must meet several criteria for effective operation of the device. At the same time that electrodes must be electrically conducting, they must be thin or porous enough to allow fuel or operating fluid to pass through them. In addition, these electrodes are often operated at high temperatures in corrosive atmospheres, so they must be sufficiently refractory to allow operation over long periods.

Previous work in this laboratory has shown that alloys of rhodium and tungsten, Rh_xW and Rh_3W , make excellent electrodes for use in AMTEC cells, where the electrodes are operated at temperatures up to 1200 K in sodium atmosphere [1, 21]. In addition, we have shown that the efficiency of such electrodes can be increased by depositing grids of molybdenum metal on the solid electrolyte before sputter depositing alloy electrodes [3]. Investigation of the properties of these electrodes led to research into the possibility of making integral grids plus electrodes of rhodium-tungsten alloy, to eliminate contact resistance between the grid lines and the electrode. Molybdenum metal makes a good current carrying grid, as the conductivity is high and it can be photodeposited in domains from an organometallic vapor by focussing UV light into the shape desired. However, the grain growth of Mo metal is relatively rapid at temperatures above 1100 K and the operating lifetime of a device may be significantly shortened if Mo grids are used [2]. Grain growth in rhodium-tungsten alloys is significantly slower than in molybdenum. While the conductivity of Rh_xW may be lower than that of Mo, the possibility of improving current collection, eliminating contact resistance between the current collection grid and the electrode, and of maintaining long operating lifetimes of electrodes in high temperature devices makes investigation of the conditions for photodeposition of Rh_xW alloys interesting.

Very little work has been done previously on photodeposition of alloys [4-7], although there are several research groups looking into photodeposition of pure metals [8-12] and there has been research into fabrication of metal alloy clusters using laser chemistry [13, 14]. In our laboratory, rhodium-tungsten alloys were made by photolytically co-depositing rhodium and tungsten from their respective organo-metallic vapors, using a single UV

source. The ratio of rhodium to tungsten was controlled by changing the temperature of the chamber holding the organometallics, to control the relative vapor pressures of the two materials. Rhodium and tungsten were both deposited from carbonyls, $RhCOCl$ and $W(CO)_6$. It has been reported that deposition from WF_6 results in purer tungsten deposits than deposition from the carbonyl [10, 12]; we found deposits from carbonyls to have inclusions of carbon, oxygen and CO, but annealing the deposited material under vacuum in the presence of a zirconium getter was sufficient to drive off inclusions.

References

1. R.M. Williams, E. Jeffries-Nakamura, M.L. Underwood, B.L. Wheeler, M. F. Loveland, S.J. Kikkert, J.L. Lamb, T. Cole, J.?, Kummer, and C.P. Bankston, *J. Electrochem. Soc.*, 136, 893 (1989).
2. M.A. Ryan, B. Jeffries-Nakamura, R.M. Williams, M.L. Underwood, D. O'Connor and S. Kikkert, *Proc. 7th Intersociety Energy Conversion Engineering Conference*, SAE, 3, 7 (1992).
3. M.A. Ryan, B. Jeffries-Nakamura, R.M. Williams, M.L. Underwood, D. O'Connor and S. Kikkert, *Proc. 26th Intersociety Energy Conversion Engineering Conference*, ANS, 5, 463 (1991).
4. P.M. George, F%. D. Dissertation, California Institute of Technology, 1971.
5. J.V. Armstrong, A.A. Burk, J.M. D. Coey and K. Moorjan, *Appl. Phys. Lett.*, 50, 1231 (1986).
6. D.K. Liu, R.J. Chin and A.L. Lai, *Chemistry of Materials*, 3, 13, (1991).
7. Y.-G. Kim, D. Byun, C. Hutchings, P.A. Dowben, H. Hejase and K. Schroeder, *J. Appl. Phys.*, 70, 6062 (1991).
8. R.R. Krchnavek, H.H. Gilgen, J.C. Chen, P.S. Shaw, T.J. Licata and R.M. Osgood Jr., *J. Vat. Sci. Technol. B*, 5, 20 (1987).
9. D.J. Ehrlich and J.Y. Tsao, *J. Vat. Sci. Technol. B*, 1, 969 (1983).
10. G.A. Kovall, J.C. Matthews, and R. Solanki, *J. Vat. Sci. Technol. A*, 6, 7353 (1988).
11. E.B. Flint, J. Messelhaeuser and H. Suhr, *Appl. Surf. Sci.*, 54, 56 (1992).
12. J.S. Cohan, H. Yuan, R.S. Williams and J.1. Zink, *Appl. Phys. Lett.*, 60, 1402 (1992).
13. S. M. Shin, C. W. Draper, M.E. Mochel and J.M. Rigsbee, *Mat. Lett.*, 3(7,8), 765, (1985).
14. J. Chaiken, M.J. Casey and M. Villarica, *J. Phys. Chem.*, 96, 3183 (1991).